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THE EFFECT OF ORIENTATION ON THE SURFACE MORPHOLOGY OF
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THE EFFECT OF ORIENTATION ON THE SURFACE MORPHOLOGY OF MERCURY CADMIUM TELLURIDE GROWN BY LPE AND VPE.

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The influence of substrate orientation on the morphology of liquid phase and vapor phase epitaxial films of mercury cadmium telluride was studied using spherically shaped {111} CdTe and CdZnTe substrates. A smooth terrace-free central region was observed, with terrace formation occurring for misorientations of greater than $0.2^\circ \pm 0.1^\circ$ from the {111} orientation. The interpretation of these results and the practical implications are discussed.

1. Introduction.

Mercury cadmium telluride is an important material for infrared detectors in the long wavelength regime. The material exists as a pseudobinary series of continuous solid solutions between HgTe, with a "band gap" 0.3 eV, to CdTe, with a band gap of 1.6 eV [1]. However, the material has properties which make it difficult to produce (see for example Ref. [2]): high mercury pressures at growth and processing temperatures, poor mechanical properties, retrograde Te solubility, high diffusion coefficients, and the difficulty of specifying the thermodynamic state of a ternary system.

Due to its importance and the difficulties in preparing material with the desired properties, many growth techniques have been developed. The most important epitaxial technique is currently

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liquid phase epitaxy (LPE), which has been developed for both Te [3-9] and Hg [10,11] melts. Another technique which has been extensively investigated is the isothermal vapor phase epitaxial technique (ISOVPE) [12-20] which takes advantage of the relatively high component vapor pressures and the high interdiffusion coefficient. The surface morphology of the layers grown by liquid phase epitaxy has been reported by many investigators [4-8]. In general, it consists of a wavy terraced structure like that shown in Fig. 1. Some workers have reported on the effect of orientation on morphology [6,7].

Many of the effects known to be important in Si and GaAs growth have not yet been investigated for the mercury cadmium telluride system. The surface morphology of III-V compound semiconductors produced by LPE and other growth techniques has been investigated by many workers. (See, for example, Ref. 21 and references therein.) In these systems it was found that for substrate orientations deviating only slightly from the low index plane, {111} or {100}, there exists a growth regime in which very flat, uniform layers are produced. However, when the substrate misorientation deviates further, a terraced surface morphology develops. The terrace-free structures have advantages which will be outlined in later sections. Bauser and Strunk [21] have investigated the effect of substrate orientation on the surface morphology of LPE GaAs layers using a spherically shaped substrate. Similar work on mercury cadmium telluride has also recently been published [7]. The advantage of this type of experiment is that a continuous range of orientations can be investigated under the same growth conditions



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in a single experiment. It was the objective of our study to perform similar experiments on the LPE and ISOVPE growth of mercury cadmium telluride to determine if there is a similar terrace-free regime in this system and, if so, the critical misorientation for the change from terrace-free to terraced growth.

2. Experimental.

Lenticular substrates were formed using the simple jig shown in Fig. 2. The rough shape is patterned using a portion of a round bottomed flask. The substrate material was {111} CdTe, both A (Cd) and B (Te) faces, for ISOVPE and {111} $\text{Cd}_{0.955}\text{Zn}_{0.045}\text{Te}$, A face, for the LPE growths. The substrates were attached to an aluminum shaft by yellow wax. The shaft in turn was held radially to the the lowest portion of the arc of the flask. Rough forming was achieved by placing a slurry of 400 grit SiC in ethylene glycol in the round bottomed flask, putting the substrate in contact with the flask/slurry, and manually turning the alumium shaft. Once the basic shape has been obtained, the shaft is removed from the slurry and the substrate surface hand finished using 600 grit paper, followed by 0.2 micron Al_2O_3 with 2% bromine in ethylene glycol. Just before growth, the substrates were etched for 2 minutes in a 4% Br in methanol solution. The resulting radius of curvature was determined by optically measuring the change in focus with lateral deviation from the center of the substrate. The results obtained for two samples are presented in Table 1 and give an indication of the technique's reproducibility.

Epitaxial layers were grown on the resulting substrates by either the LPE or ISOVPE techniques. A closed ampoule tilting LPE method was used, with the melt composition taken from the data of Harman [3] for a temperature of 500°C and a solid composition of 20% CdTe in the mercury cadmium telluride. The melt was prepared by annealing the elements in a sealed quartz ampoule at 600°C, for 12 hours. The ampoule was then quenched, opened and the source broken up for use. The same melt was not used more than twice. The ISOVPE layer that forms on the substrate as the melt is heated was removed by slightly melting back the substrate. Growth was then initiated by cooling at 0.3°C/min for 33 minutes. Some of the samples underwent a slight melt back at the end of growth prior to removal of the melt from the substrate.

ISOVPE layers were grown using a tellurium-rich mercury cadmium tellurium source which allows us to fix the surface composition of the layers [20]. The source to substrate spacing was ~ 2 cm. and growth was performed in the constant temperature zone of a sodium heat pipe at temperatures of 500, 550 and 600°C. After growth, the surface morphology of the layers was observed using an optical microscope.

3. Results.

Optical micrographs of the surface of layers grown by ISOVPE and LPE reveal a distinct terrace-free region which is flat compared to either the original radius of curvature or the terraced region, Fig. 3. The black spots on the LPE samples are retained melt, which was a problem throughout this work due, in part, to the small size of

the substrates. The density of the pyramid structures in Fig. 3a is on the order of the $1.5 \cdot 10^5$ per cm^2 . These features are only visible when the sample is tilted slightly. The center of these terrace-free regions is assumed to be exactly perpendicular to the $\{111\}$ direction. The critical misorientation at which the surface morphology changes from terrace-free to terraced is readily calculated from the radius of curvature of the sample and the diameter of the terrace-free area. Table 2 gives pertinent data for a number of ISOVPE and LPE runs. The critical degree of misorientation is found to range from 0.32° to 0.15° ; the error in the technique is estimated to be $\pm 0.1^\circ$. Notice also that the terraces in the ISOVPE material are not as wide and therefore also lower than those found in the LPE material.

4. Discussion.

The existence of distinctly different layer morphologies with different deviations from the low index growth plane closely parallels the results of experiments in the III-V semiconductors (see for example [21]). In these studies, the different morphologies were related to different growth mechanisms. In work on LPE GaAs, a one-to-one correspondence between pyramids on the central facet and dislocations has been established [21-24]. Although no similar work was done in this study, the density of pyramid structures seen on the facet in Fig. 3a, $\sim 1.5 \cdot 10^5/\text{cm}^2$, is of the same order of magnitude as the expected dislocation density, and the terrace-free growth probably proceeds by growth on dislocations which exit the free surface. On the other hand, terrace growth occurs by the

movement of terraces across the surface and by the movement of smaller steps between the terraces [21]. The terraces arise from the coalescence of monoatomic steps which are initially present as a result of the original deviation from the {111} caused by the spherical substrate shape. Bauser and Strunk [21] also observed a further terrace-free region at misorientations greater than those for terrace-free growth. However, a similar region was not observed in our work, possibly because the range of misorientations on our samples was not large enough to observe this effect.

In the III-V compounds, it has been shown that there are a number of advantages to growth in the terrace-free regime, some or all of which may apply to the mercury cadmium telluride system. The layer morphology in the terrace-free region of both systems is very flat and uniform, which offers advantages in device fabrication. Also, it has been shown in work on the III-V compounds that the terraced structure effects the distribution of dopants and impurities in the layer. For example, experiments have shown that melt impurities tend to segregate to the riser portion of the terrace and consequently preferentially deposit in these regions [21,24-27]. Since the terrace free region consists of monomolecular steps, this is not a problem in this regime. While impurity segregation was not investigated in our work, it seems probable that the same effect occurs in the mercury cadmium telluride system.

In this work this angle between terrace-free and terraced growth is calculated to be $0.2^\circ \pm 0.1^\circ$. This value seems to be relatively unaffected by the experimental parameters outlined in Table 2 and is close to that found during the LPE growth of GaAs.

0.1° [21] but is not in good agreement with the value of 0.5° reported in [7] and this disagreement may reflect the influence of some other experimental variable. Rode [28] determined this critical misorientation using a mathematical model that treats the misorientation steps as linear disruptions to the surface reconstruction which introduced surface strain.

4. Summary.

A terrace-free growth regime has been identified for the LPE and the ISOVPE growth of mercury cadmium telluride, in agreement with the results of more complete studies on the growth of III-V compound semiconductors. The critical misorientation is found to be on the order of $0.2^\circ \pm 0.1^\circ$. Assuming that the system behaves similarly to the III-V compounds, there should be advantages in layer morphology and uniformity of doping in growth from the terrace-free regime. However, growth in this regime does require accurate substrate orientation.

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Table Captions.

Table 1. Measured radii of curvature for two lenticular substrates at 1 mm. and 2 mm. away from the highest point on each sample. Two values are given at each distance, one averaged from the "north-south" directions, the other from the "east-west" directions. The radius of curvature of the pattern was 8.75 cm.

Table 2. The results and growth parameters of a series of LPE and ISOVPE experiments. The LPE layers were grown on $\text{Cd}_{0.945}\text{Zn}_{0.055}\text{Te}$ and the ISOVPE layers were grown on CdTe.

Table 1.

Sample	Radius at 1mm	Radius at 2mm
1	6.7 cm. 8.7 cm.	8.5 cm. 7.4 cm.
2	8.3 cm. 4.2 cm.	7.5 cm. 10.3 cm.

Table 1. Measured radii of curvature for two samples at 1mm and 2mm away from the highest points on the sample. Each has two values one from the "north-south" direction, the other from the "east-west" direction. The radius of curvature of the original pattern was 8.75 cm.

Table 2

LPE on CdZnTe. (4.5% ZnTe).
VPE on CdTe

Method	X Value	Critical Angle	Thickness	Temp.	Cooling Rate.	Face
LPE	0.2	0.25 +0.1°	~10 micron.	500°C	0.3°C/min.	A
LPE	0.2	0.25° "	~10 micron	500°C	0.3°C/min.	A
VPE	0.25	0.30° "	~200 micron	600°C		A
VPE	0.3	0.15° "	~12 micron	500°C		A
VPE	0.2	0.25° "	~60 micron	550°C		B
VPE	0.2	0.15° "	~60 micron	550°C		B
VPE	0.2	0.15° "	~60 micron	550°C		B

Figure Captions.

Fig. 1. Optical micrographs of the terraced surface morphology commonly found on layers grown by LPE.

Fig. 2. The jig used to form the lenticular substrates. The sample is held by yellow wax at the end of an aluminum shaft which is rotated by hand. A slurry of 400 grit SiC in ethylene glycol was used to rough form the surface. The substrates were then hand finished with 600 grit SiC followed by 0.2 micron Al_2O_3 in a 2% Br/ethylene glycol solution. Just before growth the layers were etched for 2 minutes in a 4% Br/methanol solution.

Fig. 3. Optical micrographs of ISOVPE and LPE layers grown on the lenticular substrates. a) An ISOVPE layer 200 microns thick grown at 600°C. b-d) LPE layers grown on the A (Cd) face of $\text{Cr}_{0.955}\text{Zn}_{0.045}$ at 500°C using a cooling rate of 0.3°C/min; the layers are ~10 microns thick.



Fig. 1. Optical micrographs of the terraced surface morphology commonly found on layers grown by LPE.

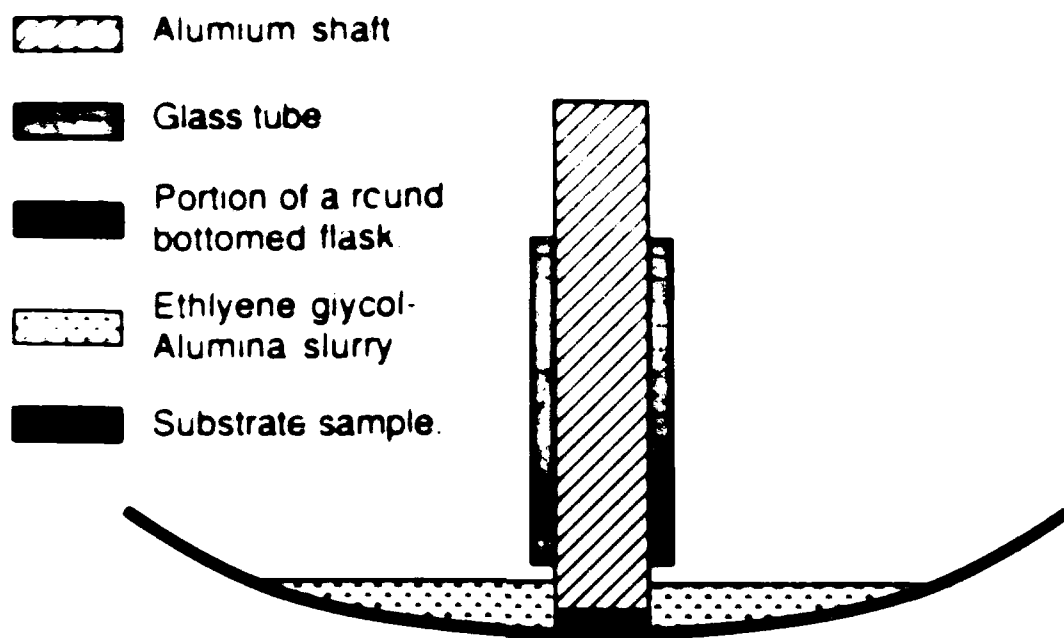


Fig. 2 The jig used to form the lenticular substrates. The sample is held by yellow wax at the end of an aluminum shaft which is rotated by hand. A slurry of 400 grit SiC in ethylene glycol was used to rough form the surface. The substrates were then hand finished with 600 grit SiC followed by 0.2 micron Al_2O_3 in a 2% Br/ethylene glycol solution. Just before growth the layers were etched for 2 minutes in a 4% Br/methanol solution.

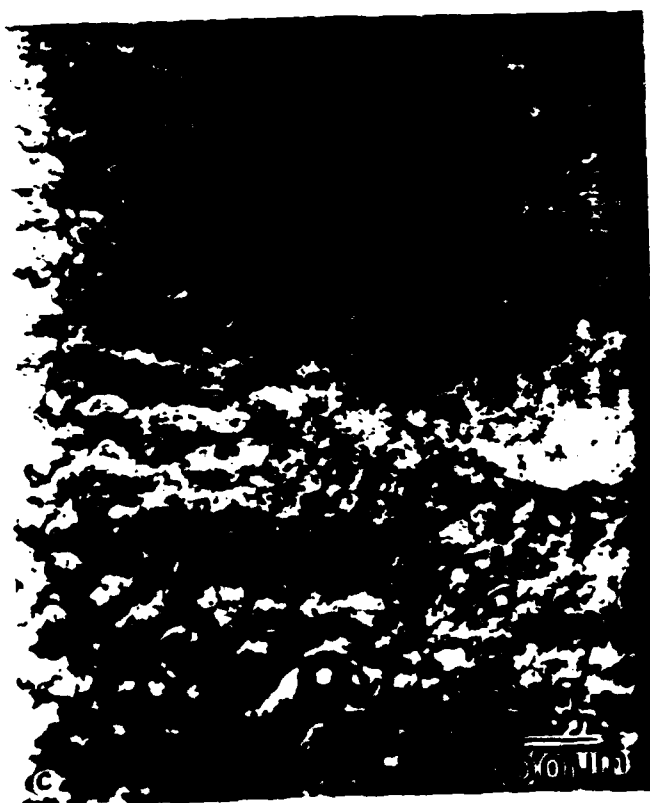


Fig. 3. Optical micrographs of ISOVPE and LPE layers grown on the lenticular substrates. a) An ISOVPE layer 200 microns thick grown at 600°C. b-d) LPE layers grown on the A (Cd) face of $\text{Cd}_{0.955}\text{Zn}_{0.045}$ at 500°C using a cooling rate of 0.3°C/min; the layers are ~10 microns thick.

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